

Preparation and Properties of High Performance Phthalide-Containing Bismaleimide Reinforced Polydicyclopentadiene

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ABSTRACT: A series of phenolphthalein-containing bismaleimide (PPBMI) reinforced polydicyclopentadiene blends (PPBMI/polyDCPD) were prepared via the ring-opening metathesis polymerization of DCPD in the presence of PPBMI. The crosslinked networks between PPBMI and polyDCPD backbones resulted in the reinforced structures. The curing behavior, thermal, and mechanical properties were investigated. Differential scanning calorimetry investigations showed the samples exhibit similar singular exothermic peak, and the exothermic peak of the PPBMI/polyDCPD blends slightly shifted to a lower temperature direction compared with the unfilled polyDCPD, meanwhile, the exothermic peak of the PPBMI/polyDCPD blends slightly shifts back to a higher temperature direction with the PPBMI content increased. Both dynamic mechanical analysis and thermo gravimetric analysis measurements revealed the optimal thermal performance of PPBMI/polyDCPD was obtained with 20 wt % loading of PPBMI. In addition, while PPBMI content increased, the weight loss peak at 100–200°C disappeared and the temperature of maximum rate of decomposition ($T_{d,max}$) increased. Moreover, bending tests showed the best mechanical performance was achieved at 5 wt % loading of PPBMI in blends. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40474.

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INTRODUCTION

Polydicyclopentadiene (polyDCPD) is a highly cross-linked thermoset polymer prepared by the ring-opening metathesis polymerization (ROMP).^{1–11} It has become more accessible due to the recent development in highly active, homogeneous Grubbs' metathesis catalysts that polymerize DCPD at low loadings of catalyst under mild conditions.¹² The excellent physical and mechanical performances of polyDCPD has allowed for many applications, such as covers on snowmobile sleds and as a protective material for hoods on semi-trucks.^{12–16}

Recently, a lot of research efforts have been dedicated to reinforce the heat-resistance and mechanical properties of materials by incorporating various fillers into the polyDCPD matrix.^{17–20} For example, Wonje and Kessler reported a significant toughness enhancement of the carbon nanotube/polyDCPD composites by incorporating norbornene functionalized multiwalled nanotubes (MWCNTs) into polyDCPD at low MWCNT loadings.¹⁷ Yoonessi et al. investigated the in situ formation of Montmorillonite (MMT)/polyDCPD composites with exfoliated morphologies only observed at low MMT loadings.^{18,19} Simons et al. studied

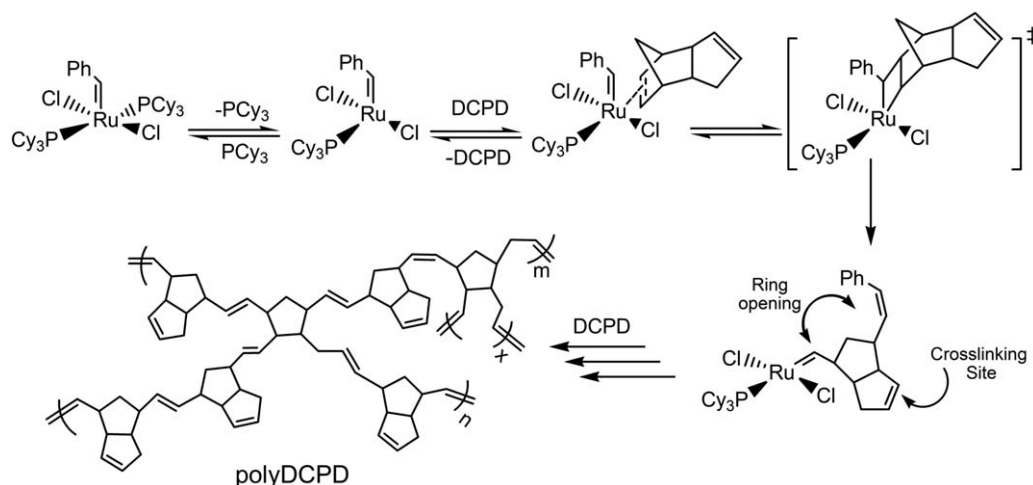
the formation of MMT/polyDCPD nanocomposites via an in situ intergallery-surface initiated ROMP of polyDCPD followed by chain cross linking and achieved up to 50% increase in the compressive Young's modulus of the composites.²⁰

Meanwhile, bismaleimides (BMIs) have gained tremendous interest from industry as a class of high-performance thermosetting polymers.^{21–23} Although a wide variety of BMIs have been studied and introduced into the marketplace, reports on BMIs reinforced polyDCPD are scarce in the literature. Herein, we report the preparation of a series of phenolphthalein-containing bismaleimide (PPBMI) reinforced polydicyclopentadiene blends (PPBMI/polyDCPD) by the ROMP over a range of PPBMI loadings. Both thermal and mechanical properties of the reinforced PPBMI/polyDCPD blends were studied and the effect of PPBMI addition was discussed.

EXPERIMENTAL

Materials

DCPD (>95%), J&K Chemical Co., Shanghai, China, was distilled before use to remove any trace impurities. Bis(tri-cyclo-hexylphosphine)benzylidene ruthenium (IV) dichloride



Scheme 1. Synthetic procedure of polyDCPD.

(first generation Grubbs' catalyst, [Ru]) was prepared as fine purple powder.²⁴ The catalyst was lyophilized,²⁵ and stored under N₂ at low temperature to minimize decomposition over time. PPBMI was synthesized according to the reported method.²⁶

Characterization

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 20DXB FTIR spectrophotometer. Samples were measured using pallets prepared by compressing the dispersed mixture of sample with KBr powder. Differential scanning calorimetry (DSC) was performed on an NETZSCH DSC 204 instrument at a heating rate of 10°C/min from room temperature to 220°C with a constant flow rate of N₂ at 20 mL/min. Thermo gravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermal analyzer. Samples (around 5 mg) were heated from room temperature to 800°C at a rate of 10°C/min, under the N₂ with a flow rate of 20 mL/min. Dynamic mechanical analysis (DMA) was performed on a TA Instruments model Q800. Samples were analyzed in the three-point bending mode with an amplitude of 20 μm at a frequency of 1.0 Hz from room temperature to 220°C at a heating rate of 3°C/min. The sample dimensions were 40 × 7 × 2 mm³. The glass transition temperature (*T_g*) was determined as the peak temperatures of the tan δ curves. The bending properties of the cured samples were evaluated from the bending strength and bending modulus according to the GB/T 9341-2008. Three-point bending tests were performed on a Universal Testing Machine (Instron 5567A) at a crosshead speed of 2 mm/min.

Polymer Synthesis

Preparation of PolyDCPD. The ROMP of neat DCPD was carried out in a mould in the presence of [Ru] (DCPD/[Ru] ratio: 1000/1) at room temperature, as shown in Scheme 1. The resulting polymer was further cured at 120°C for 2 h and then at 150°C for 2 h to complete the polymerization and evaporate the volatile substances.

Preparation of PPBMI/PolyDCPD Blend. The chemical structures of DCPD and PPBMI are shown in Figure 1. A typical procedure of preparation of the pre-cured PPBMI/polyDCPD

blend (5%) was as follows: 0.08 g of PPBMI was dissolved in CH₂Cl₂ (3 mL) at room temperature followed by addition of DCPD (1.6 g) under vigorous stirring for about 10 min and subsequently the addition of catalyst (9.964 mg, DCPD/[Ru] ratio: 1000/1). The mixtures were poured into a mould and the pre-cured PPBMI/polyDCPD blend was formed via ROMP. After ROMP, the resulting materials were further cured at 120°C for 2 h, 150°C for 2 h, 180°C for 2 h, and 200°C for 2 h. All samples were subjected to characterization within 24 h to minimize the effect of surface oxidation.²⁷

RESULTS AND DISCUSSION

Formation of PolyDCPD and PPBMI/PolyDCPD Blends

Figure 2 shows the FTIR spectra of PPBMI, polyDCPD, and PPBMI/polyDCPD blends with 5, 10, 20 wt % of PPBMI. In comparison with PPBMI, the absorption peaks at 1150 cm⁻¹ (Figure 2) disappears, indicating unsaturated double bonds of imide ring in PPBMI/polyDCPD blends has reacted substantially. In comparison with polyDCPD, the new absorption peaks at 1772 and 1709 cm⁻¹ (Figure 2) are attributed to the carbonyls of lactone groups and of maleimide groups, respectively. The vibration peaks at 1384 cm⁻¹ (C–N stretching vibration of the maleimide group), 1170 cm⁻¹ (C–O–C stretching vibration), 1500 cm⁻¹ (aromatic C=C stretching vibration), and 1241 cm⁻¹ (Ar–O–Ar stretching vibration)^{9,28} also confirmed the presence of BMI containing phthalide structure.²⁹

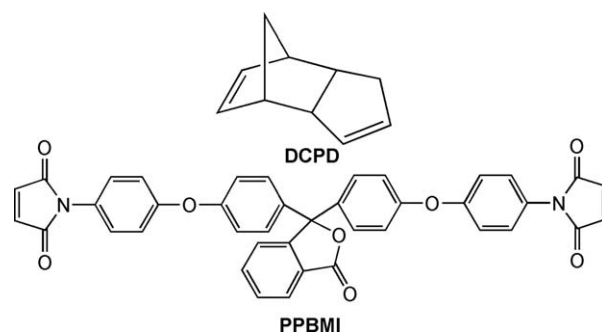


Figure 1. Chemical structures of DCPD and PPBMI.

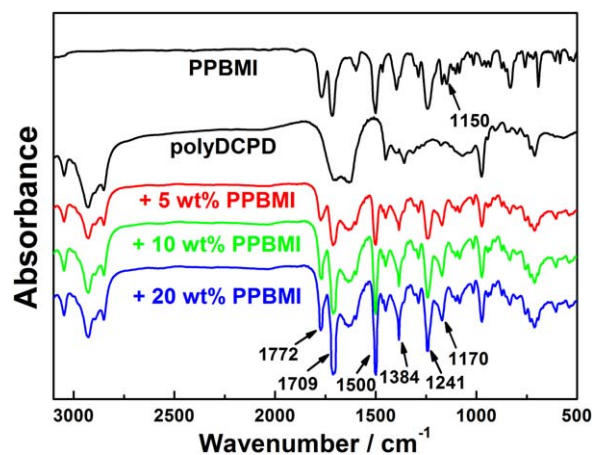


Figure 2. FTIR spectra of PPBMI, polyDCPD, and PPBMI/polyDCPD blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

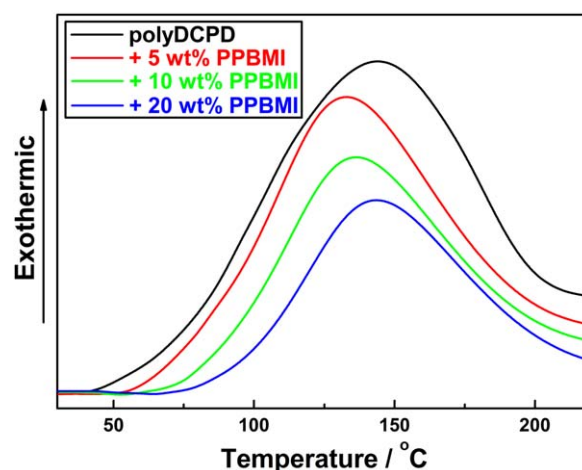


Figure 3. DSC curves of the pre-cured polyDCPD and PPBMI/polyDCPD blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

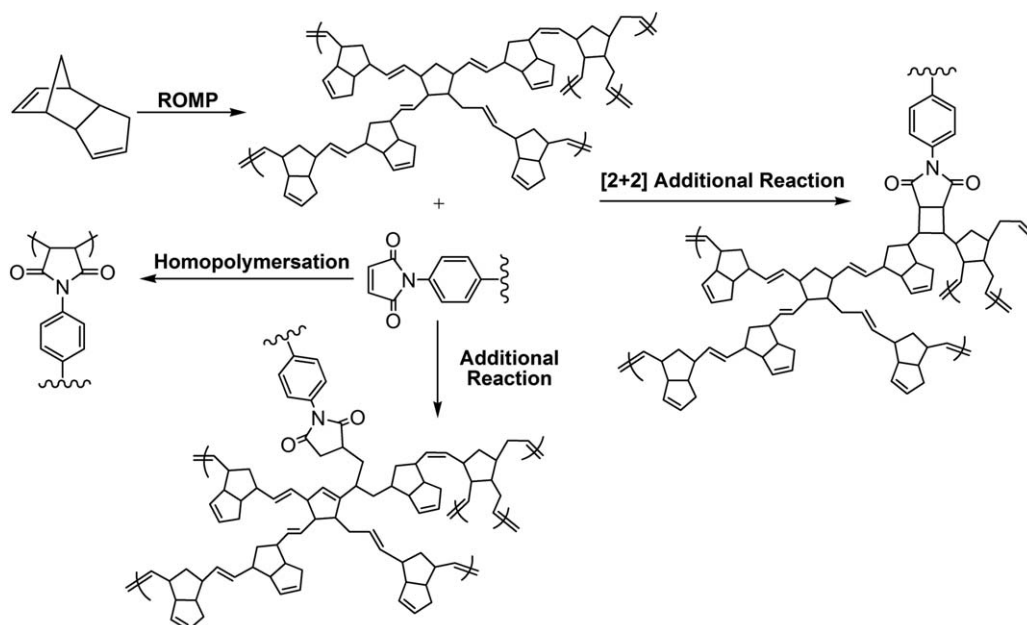
Thermal Behavior of PolyDCPD and PPBMI/PolyDCPD Blends

DSC was used to characterize the cross-linking reactions of the pre-cured PPBMI/polyDCPD blends with increasing loadings of PPBMI during the curing process. Figure 3 shows all the samples exhibit similar singular exothermic peak, indicating that each reaction (shown in Scheme 2) is almost occurs simultaneously during the curing process. Also, the exothermic peak of PPBMI/polyDCPD blends slightly shifts to a lower temperature direction compared with the unfilled polyDCPD. It is likely that the increased viscosity upon the addition of PPBMI resulted in the restricted motion of functional group. As the viscosity of PPBMI/polyDCPD blend increases, the probability of additional reaction (Scheme 2) is limited, leading to an early termination. Meanwhile, as the PPBMI content increases, the exothermic peak of the PPBMI/polyDCPD blends slightly shifts back to a

higher temperature. More phthalide side groups on PPBMI can hinder the motion of polymer chains in the blends. In addition, the electron-withdrawing carbonyl groups on PPBMI make dienophile maleimide more electron-deficient, thus more readily react with the electron-rich dienes in polyDCPD ([2 + 2] additional reaction, shown in Scheme 2). As such, the increased cross-linking density restricts the mobility of the polymer chains. Consequently, higher content of PPBMI requires higher activation temperature.

Thermal Stability of PolyDCPD and PPBMI/PolyDCPD Blends

TGA was performed to verify the thermal stability of PPBMI/polyDCPD blends and the TGA curves [Figure 4(a)] were characteristic of decomposition temperatures at 5%, 10%, 50% weight loss ($T_{d,5\%}$, $T_{d,10\%}$, $T_{d,50\%}$), temperature of maximum



Scheme 2. Possible pathways to generate crosslinked structures between PPBMI and polyDCPD.

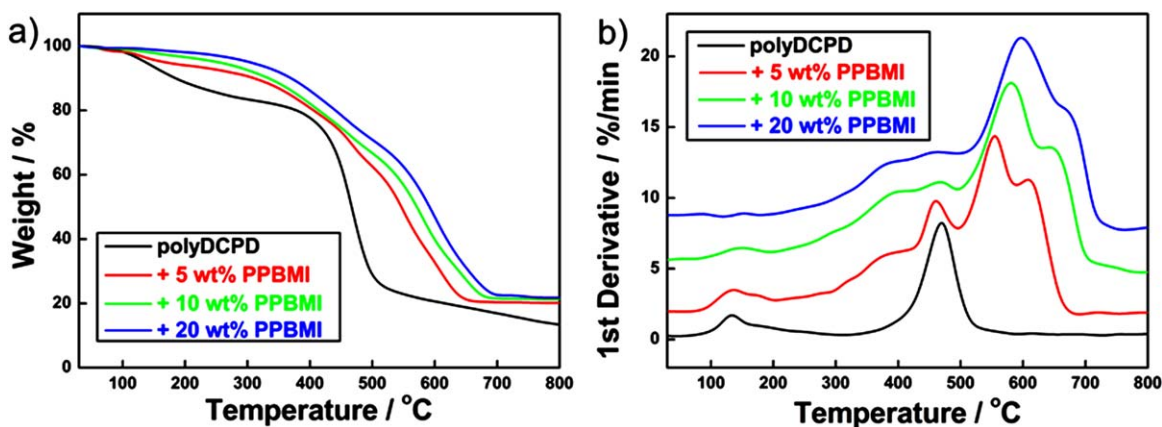


Figure 4. TGA of polyDCPD and PPBMI/polyDCPD blends: (a) TGA curves and (b) DTG curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rate of decomposition ($T_{d,max}$) [from DTG curves, shown in Figure 4(b)], and residual weight at 800°C (RW), respectively. The results of $T_{d,5\%}$, $T_{d,10\%}$, $T_{d,20\%}$, $T_{d,50\%}$, $T_{d,max}$, and RW are summarized in Table I. As shown in Table I, the increases of $T_{d,5\%}$ (ca. 150°C), $T_{d,10\%}$ (ca. 170°C), $T_{d,50\%}$ (ca. 100°C), $T_{d,max}$ (ca. 130°C), as well as RW (ca. 10%) at 20 wt % PPBMI indicate significantly enhanced thermal stability of PPBMI/polyDCPD blends compared with the unfilled polyDCPD. TGA curve of unfilled polyDCPD showed a slight weight loss between 100 and 200°C (onset is at 138.6°C) as well as a lower decomposition temperature for polyDCPD due to the presence of a small amount of cyclohexadiene monomer. The monomer can form a cyclohexadiene-rich phase in the polymerized network, which is likely to degrade at lower temperature range.²⁰ It can be observed from Figure 4(b) that as the content of PPBMI increased, the peak of weight loss at 100–200°C disappeared and $T_{d,max}$ increased, indicating thermal stability was improved. The early weight loss (400–500°C) may be attributed to the decomposition of the cured polyDCPD network. The greater proportion of polyDCPD in the PPBMI/polyDCPD blends, a given weight loss of PPBMI/polyDCPD blends can be achieved at lower temperatures. The heat resistance changes is only because of the ratio between polyDCPD and PPBMI changes, of course PPBMI has many aromatic rings, which leads to the increase in the heat resistance of the PPBMI/polyDCPD blends. Hence, the heat resistance improved is only directly related to the composition change. As shown in Figure 4(b), the main peak in black curve (450–500°C) correspond to degradation of the aliphatic chain structures derived from polyDCPD, and the shift of this peak may be attributed to the ring structures of adducts by additional reactions (Scheme 2). The new peak (553–599°C) indicates the heterocyclic structures derived from maleimide in the cured resins. In conclusion, the thermal stability was improved with the incorporation of PPBMI.

Dynamic Mechanical Properties of PolyDCPD and PPBMI/PolyDCPD Blends

The viscoelastic properties of polyDCPD and PPBMI/polyDCPD blends were characterized using DMA and the effect of PPBMI on the viscoelasticity of the blends is shown in Figure 5. The results of T_g s and storage modulus (G') at both below and

above T_g are summarized in Table II. As shown in Figure 5(a), G' s of the PPBMI/polyDCPD blends in the glassy state (30°C) significantly increase with an increasing PPBMI content, due to the incorporation of rigid heterocyclic structure into the cross-linked network.

All the cured samples studied show a single, sharp, and symmetrical relaxation peak [Figure 5(b)], which is defined as the glass transition temperature (T_g). The reasons when PPBMI/polyDCPD blends exhibit higher T_g s are twofold: the first is that the incorporation of bulky phthalide structure reduces mobility of polymer chains upon incorporation of PPBMI; the second is that PPBMI may undergo [2 + 2] additional reactions (shown in Scheme 2) with the diene moieties on polyDCPD matrix upon heating, resulting in the formation of a crosslinked structure with a higher T_g . Consequently, we use G' at $T_g + 50$ K to calculate the apparent cross-linking density ρ of the polymer network for a quantitative understanding of interactions between fillers and polymer backbone.³⁰

$$\rho = G'_{T_g+50K} / 3RT \quad (1)$$

where G'_{T_g+50K} is the storage modulus at $T_g + 50$ K, R is the gas constant, T is the absolute temperature at $T_g + 50$ K.

Table I. Parameters Obtained from TGA and DTG Measurements of Cured PolyDCPD and PPBMI/PolyDCPD Blends

Sample	$T_{d,5\%}^a$ /°C	$T_{d,10\%}^a$ /°C	$T_{d,50\%}^a$ /°C	$T_{d,max}^b$ /°C	RW ^c /%
polyDCPD	136.8	184.2	467.2	469.4	13.24
+ 5 wt % PPBMI	148.7	280.3	522.8	553.5	21.28
+ 10 wt % PPBMI	228.7	312.6	545.2	583.9	22.65
+ 20 wt % PPBMI	285.9	354.0	567.3	599.4	23.52

^aTemperature at 5%, 10%, 50% weight loss from TGA, respectively.

^bTemperature corresponding to the maximum rate of weight loss from DTG.

^cResidual weight percentage at 800°C from TGA.

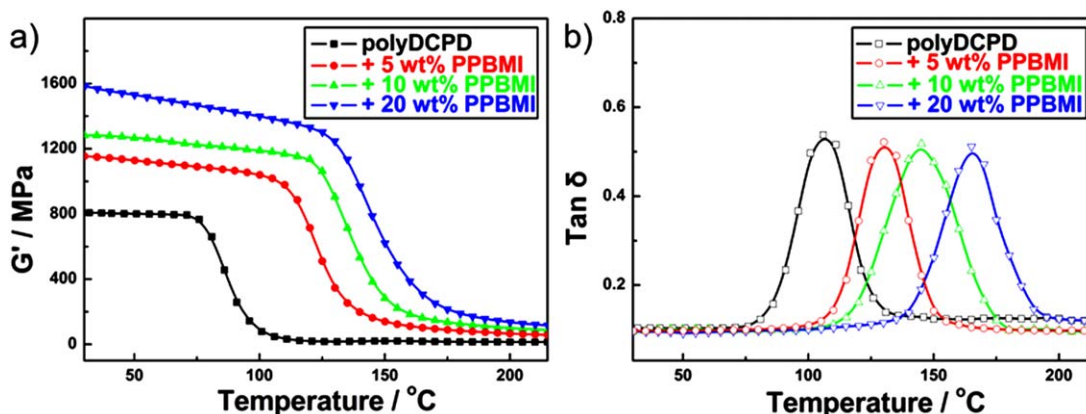


Figure 5. DMA measurements of polyDCPD and PPBMI/polyDCPD blends: (a) Storage modulus (G') and (b) $\tan \delta$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Characteristic Data of the DMA Thermograms for Cured PolyDCPD and PPBMI/PolyDCPD Blends

Sample	G'_{303K}^a /MPa	$G'_{T_g+50K}^b$ /MPa	T_g^c /MPa	$\rho \times 10^3$ ^d /mol/cm ³
polyDCPD	812.4	27.9	104.6	2.84
+ 5 wt % PPBMI	1118.6	61.8	132.3	5.44
+ 10 wt % PPBMI	1295.3	89.4	145.2	7.65
+ 20 wt % PPBMI	1590.5	121.5	177.5	9.73

^a G' at 303 K.

^b G' at $T_g + 50$ K

^c defined as the temperature of maximum $\tan \delta$.

^d calculated according to the rubber elasticity theory.

As shown in Table II, the ρ value of the PPBMI/polyDCPD blends increases with an increasing PPBMI content. The presence of PPBMI reduces the chain mobility, whereas an amount of inter-cross-linking between PPBMI and polyDCPD starts to affect the chain mobility and consequently T_g . The inter-cross-linking between the C=C bond adjacent to the electron-withdrawing groups (carboxyl) on PPBMI and the unsaturated bonds in polyDCPD network during ROMP under heating con-

ditions greatly increases the crosslinked density, thus achieving the increase of T_g .

Mechanical Properties of PolyDCPD and PPBMI/PolyDCPD Blends

To investigate the enhancement of the mechanical properties after the formation of PPBMI/polyDCPD blends, bending tests were performed and the results are shown in Figure 6. As the PPBMI content increased, the bending strength and modulus of the PPBMI/polyDCPD blends exhibit different trend. The bending strength of the blends first increased and then decreased, culminating at 5 wt % of PPBMI loading compared with the unfilled polyDCPD. At this particular position, the bending strength almost doubled. Nevertheless, the bending modulus increased with the increasing incorporation of PPBMI. The phenomena may be explained in term of two reasons. First, the addition of PPBMI leads to the increase of rigidity in the cured network. Second, the crosslinked density of the blends increased as mentioned above. Therefore, the rigidity of the blends was improved by adding PPBMI, resulting in an increase in bending modulus. When the content of PPBMI was greater than 5 wt %, the increase in viscosity of the polymer matrix resulted in local defects in the blends, which reduced the bending strength.

CONCLUSIONS

In summary, we demonstrated the successful design and fabrication of a novel PPBMI/polyDCPD blends via ROMP strategy. The effects of the PPBMI content on the thermal and mechanical properties of the blends have been systematically investigated. DSC investigations of the pre-cured polyDCPD and PPBMI/polyDCPD blends revealed that the exothermic peak of the PPBMI/polyDCPD blends slightly shifted to a lower temperature compared with the unfilled polyDCPD, but increased as the weight ratio of PPBMI increased in the PPBMI/polyDCPD blends. Meanwhile, only a single exothermic peak was observed from DSC, indicating each reaction is almost occurs simultaneously during the curing process. The thermal stabilities of the blends ($T_{d,5\%}$, $T_{d,10\%}$, $T_{d,50\%}$, $T_{d,max}$ and RW) have been enhanced with an increasing amount of PPBMI. DMA of the cured PPBMI/polyDCPD blends revealed that the glassy modulus was enhanced as the PPBMI content increased. The bending

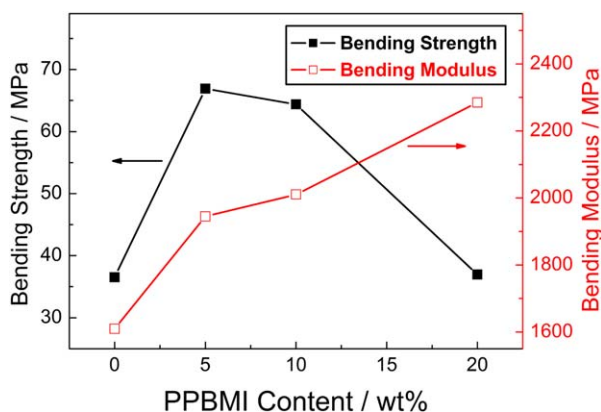


Figure 6. PPBMI effects on the bending strength and modulus of cured polyDCPD and PPBMI/polyDCPD blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

strength of the blends displayed a maximum performance at 5 wt % loading of PPBMI, whereas the bending modulus exhibited a positively correlated trend.

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